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AB INITIO AND CALPHAD THERMODYNAMICS OF MATERIALS

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Ab initio electronic structure methods can supplement CALPHAD in two major ways for subsequent applications to stability in complex alloys. The first one is rather immediate and concerns the direct input of *ab initio* energetics in CALPHAD databases. The other way, more involved, is the assessment of *ab initio* thermodynamics à la CALPHAD. It will be shown how these results can be used within CALPHAD to predict the equilibrium properties of multi-component alloys.

1. INTRODUCTION

A great deal of information about the effects of concentration and temperature on alloy properties is contained in alloy phase diagrams¹ that Massalski has called the “road maps” of the alloy designer. The modern study of alloy properties and various attempts to reach the ultimate goal of *alloys-by-design* have concentrated heavily on gaining a detailed knowledge of the electronic structure of a material and its effects on microscopic and macroscopic behaviors²⁻⁴. In addition, the study of alloy thermodynamics and statistical mechanics is most often based on the so-called Ising model. Modern theory of alloys is almost exclusively based on the mapping of the Hamiltonian describing the system at the electronic level to that associated with the Ising model^{3,4}. Despite its success limitations in the number of alloy components and the structural complexity impose severe constraints on the applicability of *ab initio* methodologies to alloys of technological interest.

Since the early 70's the so-called CALPHAD (CALculation of PhAse Diagram) approach has been very successful in describing the thermodynamics of complex alloy systems^{5,6}. A standardized framework has been established to facilitate communication among scientists, and a number of assumptions have been made to ease the calculations, most notably the assumption of the legitimacy of defining any element or alloy in any structure (the so-called “lattice stability” assumption). However its success depends on the reliability of its thermodynamic database. Hence, after recognizing the above-mentioned advantages and limitations, an efficient interface between the two approaches to alloy thermodynamics can be proposed, especially in the absence of reliable experimental data. *Ab initio* results of alloy energetics and of phase diagrams can appropriately supplement thermodynamic databases that are used within the phenomenological CALPHAD approach for predicting the stability properties of complex materials.

Following a brief overview of the first-principles and phenomenological methodologies, examples of interfacing will be presented with applications to multi-component alloys.

2. FROM ELECTRONIC HAMILTONIAN TO ISING MODEL

There are two basic questions that arise in the study of alloy phase stability: (1) What are the most probable ground states of an alloy at zero temperature, and (2) what is the evolution of these states as temperature increases? Presently, these questions are addressed through a combination of electronic structure calculations and thermodynamics based on the Ising model^{3,4}. Let us then clarify the general conceptual framework whereby the electronic Hamiltonian is mapped onto an Ising model and briefly mention specific techniques that facilitate this mapping.

Two main pathways are considered for extracting many-body interactions for alloys out of electronic structure calculations: (1) methods based on the electronic structure of random alloys, such as the Generalized Perturbation Method (GPM)³ and (2) methods based on the calculation of the electronic structure of specific ordered configurations of alloys, such as the so-called Connolly-Williams Method (CWM)⁷.

So far, all methods in category (1) have been developed within the Coherent-Potential Approximation (CPA)³ for the study of the electronic structure of substitutionally disordered alloys. In this category, it is proved that the formation energy of an alloy $A_{1-c}B_c$ in a given configuration C is expressed as

$$\Delta E_{Formation}^C = E_{Total}^C - (1 - c^C)E_{Total}^A - c^C E_{Total}^B = \Delta E_{Mix}(c^C) + \Delta E_{Ord}^C \quad (1)$$

where the mixing energy is given by

$$\Delta E_{Mix}(c^C) = E_{Total}^{CPA}(c^C) - (1 - c^C)E_{Total}^A - c^C E_{Total}^B \quad (2)$$

and the ordering energy associated with the configuration C of the alloy, to lowest order in perturbation, is written as

$$\Delta E_{Ord}^C \approx \frac{1}{2} \sum_{nm \neq n} (p_n^C - c^C)(p_m^C - c^C)V_{nm}(c^C) \quad (3)$$

where p_n^C is, at zero temperature, an occupation number equal to 0 or 1 depending on the occupation of site n by a B or A species. The total energy of the disordered state of the alloy E_{Total}^{CPA} is approximated by the CPA medium, and is concentration dependent. The expansion is derived with reference to the CPA medium, and the effective pair interactions (EPI), $V_{nm} = V_{nm}^{AA} + V_{nm}^{BB} - 2V_{nm}^{AB}$, are also concentration dependent.

Implicitly, for methods belonging to category (1), the electronic structure theory should rely on the Green function formalism, and therefore methods such as KKR and TB-LMTO² are most suitable. The limitations of the methods in this category are: (i) most codes rely on the atomic sphere approximation (ASA) for the potential function, and have been mostly developed to handle simple lattices such as fcc, bcc, and hcp, and (ii) there are still pending questions on how to handle in a first-principles way charge transfer effects.

In the methods of the second category, it is assumed (ansatz) that the formation energy of an alloy $A_{1-c}B_c$ in a given configuration C can be written as

$$\Delta E_{\text{Formation}}^C = V_0 + \sum_{\alpha} \sigma_1^C \sigma_2^C \cdots \sigma_{\alpha}^C V_{\alpha} \quad (4)$$

where the “spin” variable σ_n^C are related to the occupation number p_n^C by $\sigma_n^C = 2p_n^C - 1$.

Hence after selection of the maximum cluster (s) α , and of the ordered configurations C of the alloy, the interactions V_{α} are determined by solving a set of linear equations once the formation energies of the alloy in each configuration C has been determined with an electronic structure code. Methods in this category (2) are usually wave-based (such as Pseudo-potential, APW, ASW, LASTO, LMTO) although in principle Green functions methods can also be used. Here, the advantages are: ease of implementation, possible handling of complex structures, and accuracy afforded by full-potential methods. On the negative side, the selection *a priori* of the most pertinent set of clusters $\{\alpha\}$ and ordered configurations $\{C\}$ that will be used to set up the system of linear equations (from which the interactions will be determined) is ill defined. Note that the interactions are concentration independent except via volume effect, and usually the rate of convergence of the expansion given by Eq. (4) is rather low.

In summary, although the differences between categories (1) and (2) seem rather subtle, they both lead to a completely different way of handling the statistical mechanic part of the problem. In category (1), it is formally shown that the ordering-energy contribution to the total energy can be expanded in terms of pair and multi-site interactions, and the energy of the chemically random state of the alloy is separately calculated with the electronic structure method that can handle chemical disorder. On the other hand, in category (2), the total energy of the alloy is expanded in terms of multi-site interactions, and the energy of the disordered state is also expressed with the same interactions than those that describe order according to $\Delta E_{\text{Mix}}(c) = \Delta E_{\text{Formation}}^{\text{Dis}}(c) = V_0 + \sum_{\alpha} (2c - 1)^{\alpha} V_{\alpha}$.

3. CALPHAD THERMODYNAMICS

In the CALPHAD approach^{5,6}, the Gibbs energy of each individual phases is modeled, and the model parameters are collected in a thermodynamic database. It is the modeling of the Gibbs energy of individual phases and the coupling of phase diagram and thermochemistry that make the CALPHAD a powerful technique in computational thermodynamics of multi-component materials. For pure elements and stoichiometric compounds, the most commonly used model is the one suggested by the Scientific Group Thermodata Europe (SGTE)⁸ that has the following form (for simplicity, the pressure dependence and the magnetic contribution are not shown here),

$$G_m - H_m^{\text{SER}} = a + bT + cT \ln(T) + \sum_i d_i T^i \quad (5)$$

The left-hand side of Eq. (5) is defined as the Gibbs energy relative to a standard element reference state (SER), where H_m^{SER} is the enthalpy of the element in its stable state at 298.15 K and 10^5 Pa of pressure. Coefficients, a, b, c, and d_i are the model parameters.

The SGTE data for all the pure elements of the periodic table have been compiled by Dinsdale⁹.

For multi-component solution phases, the Gibbs energy has the following general expression⁶,

$$G = G^o + G_{mix}^{ideal} + G_{mix}^{xs} \quad (6)$$

where G^o is the contribution from the mechanical mixing of the pure components, G_{mix}^{ideal} is the ideal mixing contribution, and G_{mix}^{xs} is the excess Gibbs energy of mixing due to non-ideal interactions. Sub-lattice models have been widely used to describe solution phases⁶. For example, for a simple phase with two sub-lattices in an A-B binary system with the two components entering both sub-lattices, the sub-lattice model is written as $(A,B)_p(A,B)_q$, where subscripts p and q denote the number of sites of each sub-lattice. More specifically, the three terms in Eq. (6) are written as,

$$G^o = y_A^I y_A^II G_{A:A}^o + y_A^I y_B^II G_{A:B}^o + y_B^I y_A^II G_{B:A}^o + y_B^I y_B^II G_{B:B}^o \quad (7)$$

$$G_{mix}^{ideal} = pRT \left(y_A^I \ln y_A^I + y_B^I \ln y_B^I \right) + qRT \left(y_A^II \ln y_A^II + y_B^II \ln y_B^II \right) \quad (8)$$

$$G_{mix}^{xs} = y_A^I y_B^II \left(y_A^I \sum_{k=0} L_{A,B:A}^k (y_A^I - y_B^I)^k + y_B^II \sum_{k=0} L_{A,B:B}^k (y_A^I - y_B^I)^k \right) \\ + y_A^II y_B^I \left(y_A^II \sum_{k=0} L_{A:A,B}^k (y_A^II - y_B^II)^k + y_B^I \sum_{k=0} L_{B:A,B}^k (y_A^II - y_B^II)^k \right) \quad (9)$$

where y^I and y^{II} are the site fractions of A or B in the first and second sub-lattices, respectively. $G_{I:J}^o$ is the Gibbs energy of the compound $I_p J_q$, expressed by Eq. (7). $L_{A,B:*}^k$ ($L_{*,A,B}^k$) is the k^{th} -order interaction parameter between component A and B in the first (second) sub-lattice. In this notation, a colon separates components occupying different sub-lattices, and a comma separates interacting components in the same sub-lattice. These equations can be generalized for phases with multi-components and multi-sub-lattices, and they reduce to a random substitutional model when there is only one sub-lattice.

For a multi-component solution in a particular phase Φ described with a single sub-lattice model, the three contributions to the total Gibbs energy reduce to⁶:

$$\begin{aligned} \Phi G^o &= \sum_I c_I \Phi G_I^o \\ \Phi G_{mix}^{ideal} &= RT \sum_I c_I \ln c_I \\ \Phi G_{mix}^{xs} &= \sum_I \sum_{J>I} c_I c_J \sum_k \Phi L_{I,J}^k (c_I - c_J)^k \end{aligned} \quad (10)$$

where the molar excess Gibbs energy of mixing is expressed by a Redlich-Kister expansion⁶. In these expressions c_I is the composition of the alloy in species I, and $L_{I,J}^k$ is a k^{th} -order binary interaction parameter between species I and J that is expressed as a polynomial in temperature T. Note that in both sets of expressions the excess Gibbs

energy due to non-ideal contributions is expressed within the Muggianu approximation¹¹.

Thermodynamic modeling begins with the evaluation of the thermodynamic descriptions of unary and binary systems. By combining the thermodynamic descriptions of constitutive binary systems and ternary experimental data, a thermodynamic description of ternary systems is developed, and so forth for higher-order component alloys.

As said in the introduction *ab initio* output, such as structural energies, heats of formation, heats of transformation, elastic and magnetic properties, can be used in a CALPHAD description of alloy properties. This is the most immediate application of *ab initio* to CALPHAD. Furthermore, when the link between *ab initio* electronic structure calculations and statistical mechanics has been achieved, the information on thermodynamic functions as function of alloy composition and temperature, and phase diagram results are available. This can be included in a theoretical assessment “à la CALPHAD” of the thermo-chemistry of alloys (the same way an assessment is carried within CALPHAD solely based on experimental data). This input from *ab initio* adds to the capabilities of CALPHAD to predict the thermodynamic properties of complex multi-component alloys.

4. APPLICATIONS

The results of the *ab initio* calculations presented in this section were carried out on the basis of the charge self-consistent fully relativistic version of the TB-LMTO-CPA method within the atomic-sphere approximation and the local-density approximation (LDA) of density functional theory¹². The effects of statistical fluctuations away from the CPA³ average medium have been studied with the GPM^{3,4} that leads to uniquely defined, concentration-dependent EPI. When used in conjunction with a generalized mean-field statistical treatment such as the cluster variation method (CVM)¹³, alloy phase diagrams⁴ can be predicted.

4.1. *Ab initio* formation energies in CALPHAD

In CALPHAD databases no energetic information was available for the ordered Ni₂Cr phase (C11_b or oP6) that is observed experimentally. In addition since the goal was to describe the ternary Ni-Cr-Mo-W system, data on the formation energy of the hypothetical ordered Ni₂Mo and Ni₂W phases was required. Hence, *ab initio* calculations were performed for these three compounds and the results are shown in Fig. 1.

For Ni-Cr-Mo-W the ordered phase was treated within a two-sub-lattice model (cf. section 3) with Cr, Mo, and W on one sub-lattice, and Mo, Ni, W on the other sub-lattice. The compound phase parameters (with temperature T in K, and the energies in J/mol, with one atom per mole) are defined as follows (note that the parameters not included in the following are set to zero):

$$\begin{aligned}
 \Delta G_{\text{Cr:Mo}}^{\text{fcc-oP6}} &= \Delta G_{\text{Mo:Mo}}^{\text{fcc-oP6}} = \Delta G_{\text{W:Mo}}^{\text{fcc-oP6}} = +6,000 & \Delta G_{\text{Cr:Ni}}^{\text{fcc-oP6}} &= -7,095 - 5.6 \cdot T \\
 \Delta G_{\text{Mo:Ni}}^{\text{fcc-oP6}} &= +1,000 & \Delta G_{\text{W:Ni}}^{\text{fcc-oP6}} &= +10,000 & (11) \\
 {}^0L_{\text{Cr:Mo,Ni}}^{\text{fcc-oP6}} &= -80,000 & {}^0L_{\text{Cr,Mo:Ni}}^{\text{fcc-oP6}} &= -11,000 & {}^0L_{\text{Cr,W,Ni}}^{\text{fcc-oP6}} &= -55,000 & {}^0L_{\text{Cr,W:Ni}}^{\text{fcc-oP6}} &= -8,000
 \end{aligned}$$

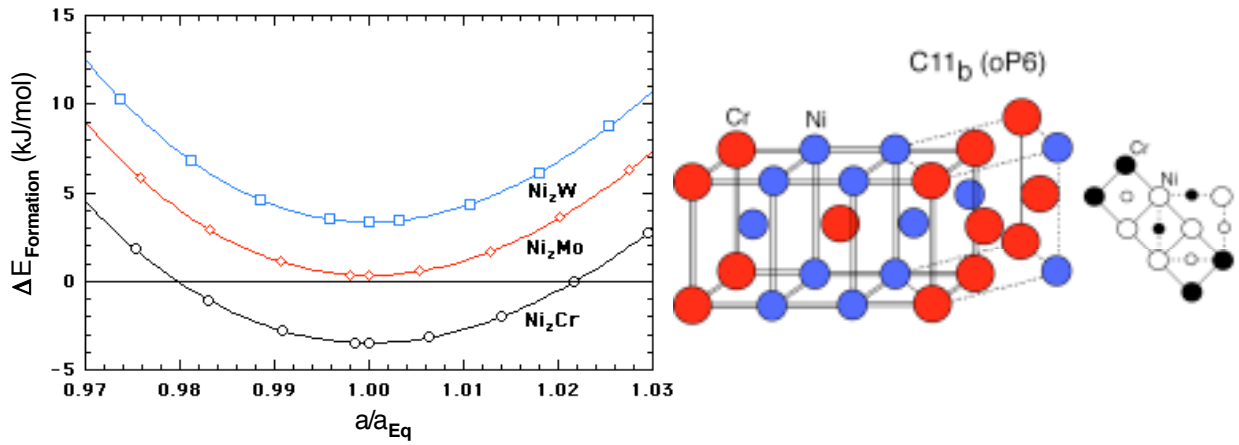


Figure 1. Total energy (in kJ/mol) versus normalized lattice parameter (*i.e.*, a/a_{Eq} , where a is the lattice parameter and a_{Eq} is the equilibrium lattice parameter) for Ni_2Cr , Ni_2Mo , and Ni_2W of Ni_2Cr -type ($C11_b$ or $oP6$ shown on the right). The zero of energy is taken as the concentration weighted average of the total energies of fcc Ni and bcc Cr (or Mo, W).

To adjust the experimental information on Ni_2Cr with already available thermodynamic data in the CALPHAD database, the heat of formation of Ni_2Cr became -7,095 J/mol (instead of -4,187 J/mol). The data for Mo-Ni and W-Ni account for the *ab initio* results that indicate that Ni_2Mo is barely stable whereas Ni_2W is unstable (leading to a positive heat of formation of +10,000 J/mol). Finally the description of Mo on both sub-lattices is contained in the two Redlich-Kister parameters ${}^0L^{fcc-oP6}$. Their values have been adjusted to allow Mo to be located on the two sub-lattices, to widen the domain of stability of the ordered phase in accordance with the results of Karmazin *et al.*¹⁴, and at the same time to account for the effect of Mo addition on the order-disorder transition temperature¹⁴.

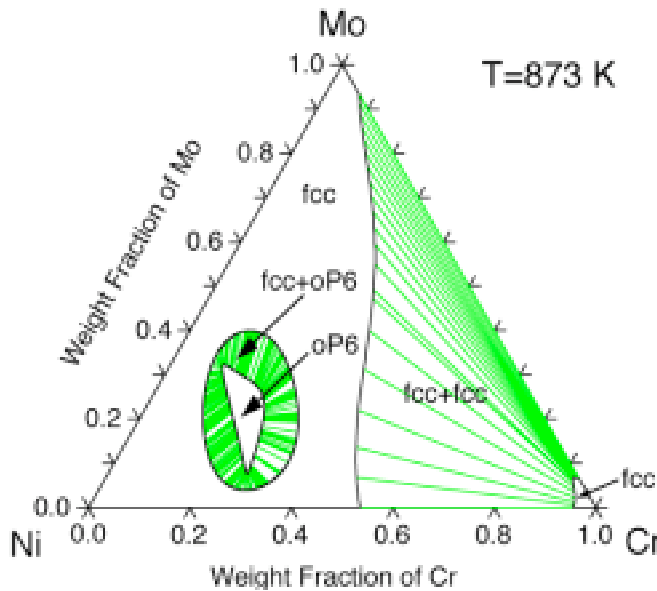


Figure 2. Calculated isothermal section of the Ni-Cr-Mo phase diagram at 873 K. Only the fcc matrix and the oP6-ordered phase are considered for this set of calculations.

By limiting the analysis to the fcc matrix and the oP6 ordered phase (*i.e.*, with all other phases suspended), isothermal sections of the Ni-Cr-Mo phase diagram were calculated.

The results presented in Fig. 2 at $T=873$ K show the domain of stability of the oP6 phase in a diagram that would have only indicated a fcc-solid solution without *ab initio* input.

4.2. *Ab Initio* phase diagrams in CALPHAD

The output *ab initio* thermodynamics can be converted to a Redlich-Kister/Bragg-Williams format with an acceptable level of accuracy. The results of this conversion can then be combined with those of an existing CALPHAD thermodynamic database. The procedure is illustrated in the case of the ternary Mo-Ta-W alloys.

The Gibbs energies and molar enthalpies of formation of the bcc phases as well as the solid-state portion of the phase diagram obtained from CVM¹³ with the energetics calculated from *ab initio* were obtained for the three binaries. The CVM results predict the existence of a domain of stability of B2 for Ta-W¹⁵ and Ta-Mo¹⁶, whereas for Mo-W¹⁶, for all practical purposes, a solid solution is found in the entire composition range (since the mixing and ordering energies are less than 1.3 kJ/mol). This information was used for the CALPHAD fitting procedure, performed with the PARROT module of Thermo-Calc¹⁷. To match the energetics between the bcc-solid solution and the liquid phase we assumed that the Redlich-Kister parameters of the two phases were the same except for an extra contribution to ${}^0L_{Ta,W}^{Liq}$ for the sake of simplicity. Hence, this procedure ensured that the T_0 location associated with the two phases at equi-atomic composition was compatible with the experimentally assessed liquidus-solidus lines¹.

The Gibbs energy differences between the CVM and CALPHAD results from 800 K to 3000 K are less than 2 %. As a consequence the CALPHAD phase diagrams of Ta-W¹⁸ and Ta-Mo¹⁹ displayed in Fig. 3 compare extremely well with those from *ab initio*.

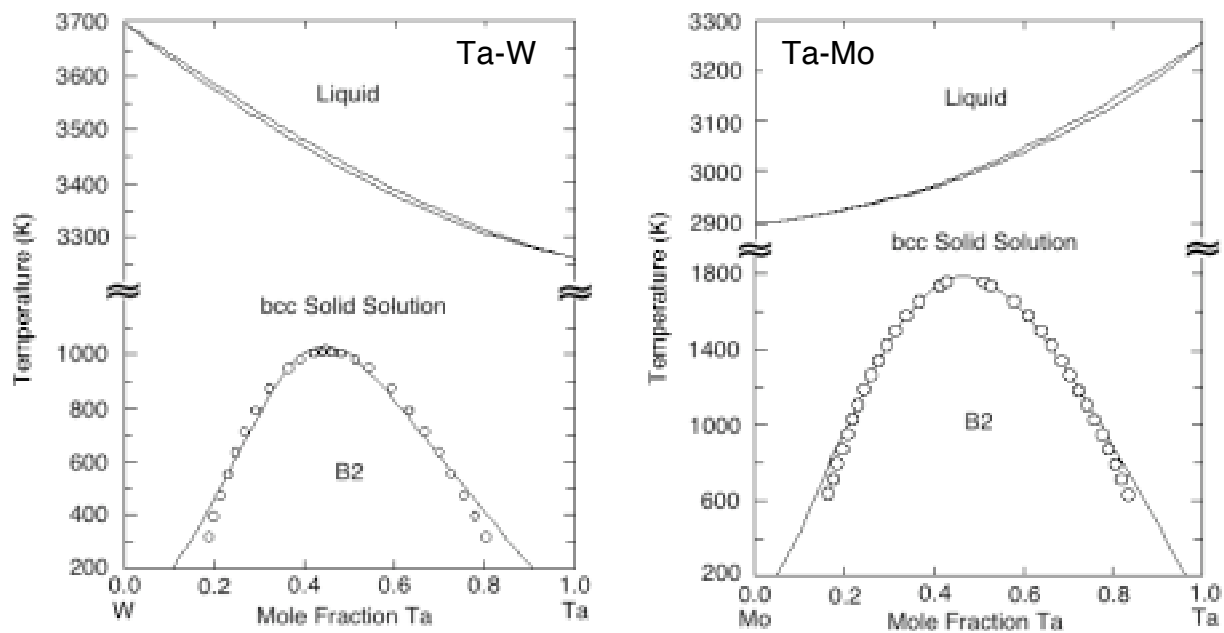


Figure 3. Ta-W and Ta-Mo phase diagrams obtained from the application of Thermo-Calc to CALPHAD (solid line), and compared with the CVM results (data points).

Because the Redlich-Kister parameters, pL with $p>0$ in Eq. (10), are made temperature dependent and the excess Gibbs energy depends on alloy composition, it is equivalent to considering interactions that are temperature and concentration dependent in an Ising model. This versatility adds to the Bragg-Williams solution to the chemical order problem and is responsible for the agreement.

This conversion provides a robust and yet simple scheme that is consistent with standard assessment of multi-component alloy phase diagrams. As an illustration, let us consider the ternary Mo-Ta-W alloy¹⁹. The solid portion of the assessed phase diagrams¹ for the three binaries only indicates a single domain of stability for the bcc solid solution. From the *ab initio*-thermodynamic results for the three binaries represented in a CALPHAD format, CALPHAD-based calculations were performed within the Muggianu description¹¹ for the ternary Mo-Ta-W system, see Eq. (10), with no extra ternary parameters. Isothermal sections of the ternary Mo-Ta-W alloy are shown in Fig. 4a. Calculations were also carried out for the ternary system with a CVM approach in the irregular tetrahedron approximation, with the *ab initio* energetics of the binaries and no additional ternary interactions. The results are shown in Fig. 4b. Note that the CALPHAD approach slightly overestimates the maximum critical order-disorder (B2-A2 or bcc) temperature because of the Bragg-Williams approximation. As a reminder, the full CALPHAD treatment (i.e., with no input from *ab initio*) would only reveal a domain of stability of the bcc solid solution.

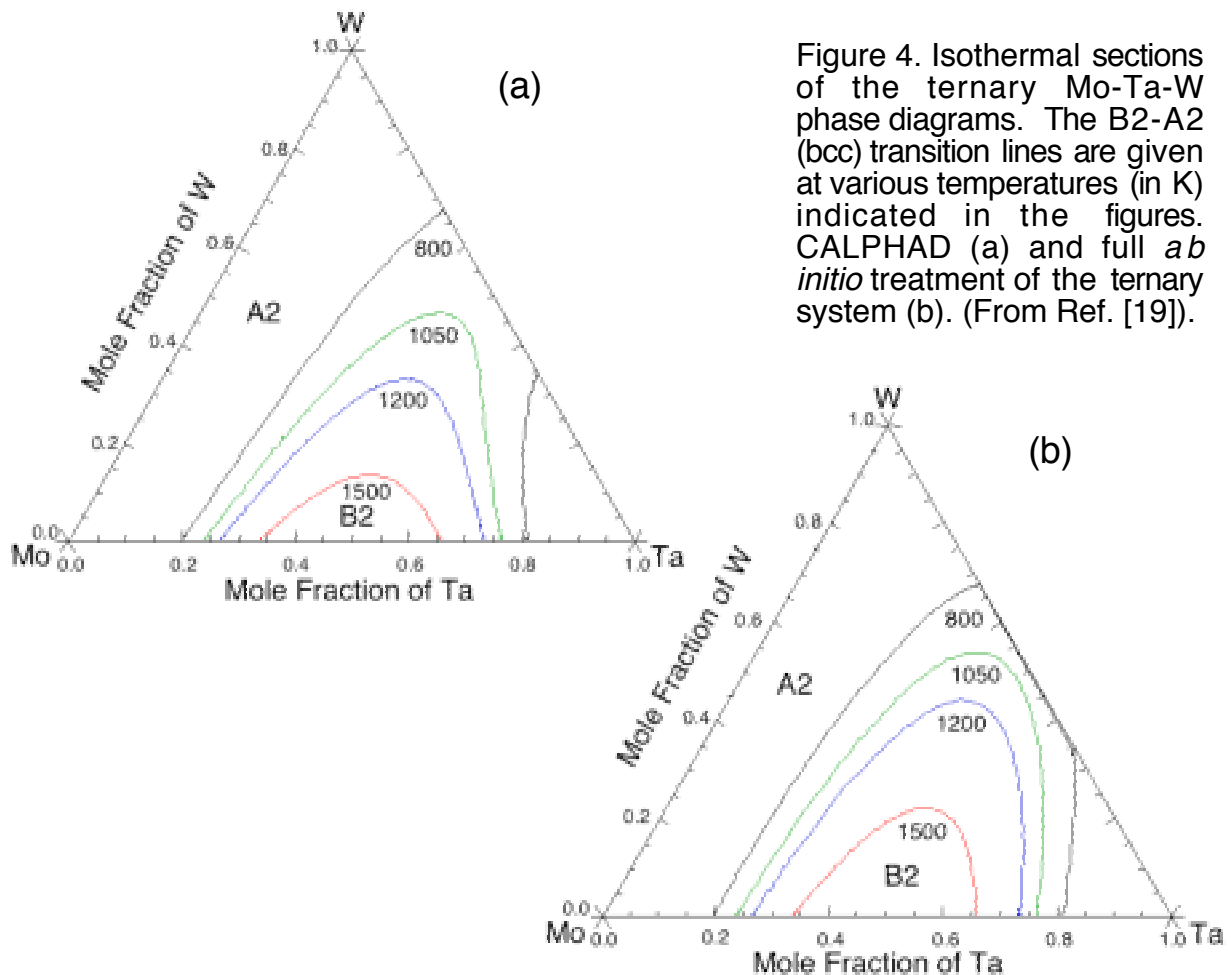


Figure 4. Isothermal sections of the ternary Mo-Ta-W phase diagrams. The B2-A2 (bcc) transition lines are given at various temperatures (in K) indicated in the figures. CALPHAD (a) and full *ab initio* treatment of the ternary system (b). (From Ref. [19]).

In the example of the ternary Mo-Ta-W system for which experimental information was unavailable, it was shown that the power of *ab initio* calculations could advantageously supplement the CALPHAD database to predict alloy stability in higher-order component alloys.

5. CONCLUSION

A wide variety of electronic structure codes are now available to obtain a wealth of results (not just energies!), and to provide an understanding at the atomistic level of the intricate relation between electronic structure properties and stability and order in alloys. *Ab initio* studies also reveal trends that exist as functions of the number of valence electrons and the difference in the numbers of valence electrons. Any electronic structure code should be tested against a broad range of experimental data spanning from structural information to results from various spectroscopies that probe the electronic properties, elastic properties, magnetism (if any), *etc.*, so that a level of confidence can be established on the legitimacy of the various approximations (or constraints).

Energetics obtained from *ab initio* calculations can be readily input in thermo-chemical databases used in conjunction with CALPHAD, and be considered as educated starting guesses for further assessment of phase diagrams.

Ab initio phase diagram results can also be treated as experimental results and be assessed “à la CALPHAD” to enhance the predictive capabilities in an approach that is otherwise phenomenological in essence, and when experimental data are lacking.

The two links that have been discussed between *ab initio* and CALPHAD can also be used in a reverse mode to test, validate, and challenge the approximations built in any first-principles approach to alloy stability and order.

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